



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 298 185 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**02.04.2003 Bulletin 2003/14**

(51) Int Cl.7: **C10G 9/16**

(21) Application number: **01203659.6**

(22) Date of filing: **27.09.2001**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**  
Designated Extension States:  
**AL LT LV MK RO SI**

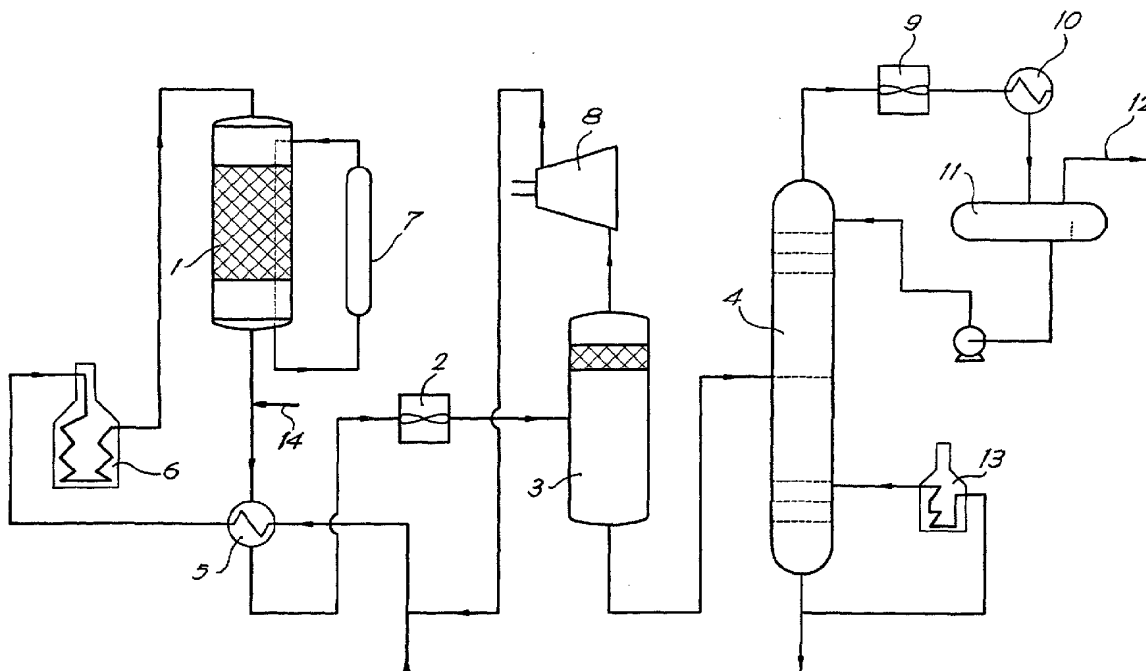
(72) Inventor: **Vercammen, Fernand**  
**2460 kasterlee (BE)**

(74) Representative: **Donné, Eddy**  
**Bureau M.F.J. Bockstael nv**  
**Arenbergstraat 13**  
**2000 Antwerpen (BE)**

(71) Applicant: **Vercammen, Fernand**  
**2460 kasterlee (BE)**

(54) **Method for preventing fouling and corrosion caused by ammonium chloride and ammonium sulphates**

(57) Method for preventing fouling and corrosion caused by ammonium chloride and ammonium sulphates, characterised in that it comprises injecting as an additive a choline or a derivative thereof.



EP 1 298 185 A1

## Description

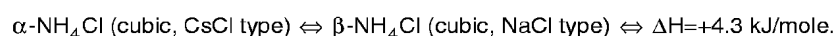
[0001] This invention concerns a method for preventing fouling and corrosion caused by ammonium chloride and ammonium sulphates particularly formed or present in crude oil refinery processes.

[0002] From literature and field experience it is known that ammonium chloride and ammonium sulphates are corrosive, as gas, as solid, or in solution. Ammonium chloride is acidic, complexes metal ions, and contains the corrosive chloride ion. Ammonium sulphate is acidic and complexes metal ions. Therefore, corrosion protection is one of the major concerns in refinery operations where ammonium chloride and ammonium sulphates are generated through the process itself or being imported from other units with the feedstock. Several forms of corrosion are observed.

[0003] The extent of corrosion largely depends on, for example the  $\text{NH}_4\text{Cl}$  concentration, the pH, and the temperature. Equipment made from iron, aluminium, lead, stainless steels, or non ferrous metals is especially prone to stress corrosion cracking.

[0004] Solid ammonium chloride has a specific gravity  $d_4^{20}$  of 1,530. Its average specific heat  $c_p$  between 298 and 372 °K is 1,63 kJ/kg.

[0005] Ammonium chloride has two modifications. The transformation between the two is reversible at 457,6 °K (184.5°C):



[0006] The  $\alpha$  modification is the one stable at room temperature.  $\beta\text{-NH}_4\text{Cl}$  melts at 793,2 °K under 3,45 MPa; it sublimates at atmospheric pressure. In fact,  $\text{NH}_4\text{Cl}$  is quite volatile at lower temperatures, dissociating into  $\text{NH}_3$  and  $\text{HCl}$ :

T, °K	523,2	543,2	563,2	583,2	603,2	611,2
p, kPa	6,6	13,0	24,7	45,5	81,4	101,3

[0007] The solubility of  $\text{NH}_4\text{Cl}$  in water increases with temperature:

T, °K	273,2	293,2	313,2	333,2	353,2	373,2	389,2
c, wt%	22,9	27,2	31,5	35,6	39,7	43,6	46,6

[0008] The partial pressures of saturated  $\text{NH}_4\text{Cl}$  solutions show that  $\text{NH}_4\text{Cl}$  is weakly hygroscopic :

T, °K	283,2	293,2	303,2	313,2	323,2	389,2
p, kPa	1,0	1,9	3,3	5,4	8,8	101,3

[0009] Less known, is that ammonium sulphate and, in particular ammonium bisulphate, also precipitates as a foulant and corrosive agent in refinery processes as described before.

[0010] Ammonium sulphates cannot be melted at atmospheric pressure without decomposition, releasing ammonia and leaving bisulphate. However, the ammonia vapour pressure of pure, anhydrous ammonium sulphates are effectively zero up to 80 °C. Above 300 °C, decomposition gives  $\text{N}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ , and  $\text{H}_2\text{O}$  in addition to ammonia.

[0011] The salts do not form hydrates. The solubility of ammonium sulphates is reduced considerably by addition of ammonia: At 10 °C, from 73 g  $(\text{NH}_4)_2\text{SO}_4$  in 100 g of water, nearly linearly, to 18 g salt in 100 g of 24.5% aqueous ammonia.

[0012] The fouling and corrosion phenomena in the crude oil refinery processes, such as hydro-treating, hydro-cracking, catalytic reforming, catalytic cracking, but not limiting to these processes, is a great concern of the operator. A typical conversion refinery is spending a lot of money for maintenance, renewal of equipment, while the downtime of the unit is accounting for a substantial loss in production and profits.

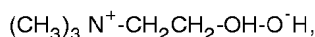
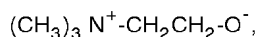
[0013] Equipment being exposed to ammonium chloride fouling has to be thoroughly washed with an alkaline solution, to avoid stress-corrosion cracking. Ammonium bisulphate is depositing at higher temperatures as compared to ammonium chloride, and therefore, more difficult to remove by washing with water.

[0014] Typical areas for fouling and corrosion are, for example but not limiting, feed-effluent exchangers from reactors and distillation columns, recycle gas compressors transporting hydrogen containing ammonium chloride to the reactor feedstock, stabiliser, reboiler and overhead section.

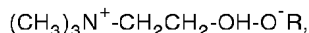
[0015] The invention aims to provide a method for preventing fouling and corrosion caused by ammonium chloride

and ammonium sulphates.

**[0016]** According to the invention this aim is reached by injecting as an additive a choline or a derivative thereof, more specifically a derivative with one of the following general formulas:



and



wherein R = an alkyl with C<sub>1</sub>-C<sub>20</sub>.

**[0017]** Choline, known as choline base, is a liquid strong organic base: trimethyl(2-hydroxyethyl)ammoniumhydroxide having the general formula  $[(\text{CH}_3)_3\text{N}^+\text{-CH}_2\text{CH}_2\text{-OH}]\text{-OH}^-$ . It is usually not encountered as a free base, but as a salt or derivative such as choline hydroxyde, choline chloride, choline hydrogen tartrate, tricholine citrate which are commercially available and are used in medical applications and as nutrients.

**[0018]** By injection, the additive to the process flow, the ammonium chloride and ammonium sulphates are converted into non-corrosive and non-depositing components which are surprisingly liquid and neutral, freeing the various processes from fouling and corrosion created by ammonium chloride and ammonium sulphates.

**[0019]** It is known to add amines for corrosion inhibition, but these amines form a salt which remains sticky (form a paste) or solid, and when dissolved in water show an acidic pH value (< 7,0).

**[0020]** Also surprisingly, the chloride salt formed with the additive is a volatile chloride which can be removed from the process stream by stripping or gas recycling.

**[0021]** The method is particularly useful in crude oil refinery processes.

**[0022]** In a particular unit called catalytic reformer, the volatile formed component can be recycled through the hydrogen recycle gas stream to the reactor, thereby reducing the amount of organic chloride used for activation of the reformer catalyst. Up to 40 % savings in organic chloride product has been demonstrated in a pilot plant.

**[0023]** The quantity of additive injected, is preferably situated between 1 ppm and 5000 ppm, dosed on the amount of chlorides or sulphates present.

**[0024]** The additive is preferably injected as a solution containing 1% weight to 65 % weight additive in a solvent, for example an alcohol, preferably an aliphatic alcohol having up to 8 C atoms, an ether, an aromatic or water. The concentration of the choline base of choline derivative in the solution may for example vary from 1 % to 65 % in weight. A stabiliser may be added such as for example an unsubstituted hydroxylamine salt.

**[0025]** The additive is usually fed upstream the formation or deposition of ammonium chloride and ammonium sulphates to prevent formation of ammonium chloride and ammonium sulphates or to convert ammonium chloride and ammonium sulphates to other components.

**[0026]** The additive may also be fed downstream the formation or deposition of ammonium chloride and ammonium sulphates to convert ammonium chloride and ammonium sulphates to other components, but it is not limiting its feeding point to a particular place in the process.

The following example explains the invention:

**[0027]** A pilot catalytic reformer with continuous regeneration catalyst, shown in the enclosed figure, is used to test the performance of the additive at various levels of ammonia and chloride. As shown in the figure, this reformer comprises mainly a reactor 1, an airfin cooler 2, a separator 3 and a stabiliser 4 mounted in series.

**[0028]** The feedstock is fed to the reactor 1 over a feed-effluent exchanger 5 and a catalytic reformer furnace 6.

**[0029]** The feedstock consists of a typical heavy full range naphta with varying levels of ammonia and with an end boiling point of 192°C. The hydrogen to hydrocarbon molar ratio is 4,0 operating at an outlet temperature of 510 °C and the pressure in the reactor 1 is 9,8 bar.

**[0030]** The catalyst used is R 22 from UOP and is continuously recycled as shown by reference numeral 7. The organic chloride catalyst activator is fed at a rate of 2 ppm. The conditions in the reactor 1 were governed to maintain a reformat RON (Research Octane Number) of 98.

**[0031]** The gases from the separator 3 are compressed in compressor 8 and reintroduced in the feed stock. The liquid from the separator 4 is fed to the reformat stabiliser 4. The gases are cooled in airfin cooler 9 followed by a

## EP 1 298 185 A1

water cooler 10 and then collected in an overhead accumulator 11. The remaining gases are evacuated via the off-gas 12, while the liquid is returned as a reflux to the upper part of the stabiliser 4. The reformat is evacuated from the bottom of the stabiliser 4 and part of it is recycled over a stabiliser reboiler furnace 13.

Blank test :						
Product Analysis	Feedstock in ppm	Reactor Outlet Reformate ppm	Stabiliser feed Ppm	Recycle gas Ppm	Stabiliser off-gas Ppm	Stabilised reformat ppm
NH <sub>3</sub>	1,5	-	-	-	-	-
HCl	0,5	-	-	-	-	-
NH <sub>4</sub> Cl	-	2,5	1,3	0,3	< 0,1	< 0,1
RCI	2*	-	-	-	-	-

\*Organic chloride fed to reactor

Analysis/ Observation	Hydrogen recycle airfin cooler	Stabiliser overhead airfin cooler	Stabiliser overhead water cooler	Stabiliser overhead accumulator
Corrosion rate	0,559 mmpy (22 mpy)	1,143 mmpy (45 mpy)	1,727 mmpy (68 mpy)	0,940 mmpy (37 mpy)
Salt deposition	Yes	Yes	Yes	No
PH saturated water	2,7	2,3	1,7	3,5

Test data :

**[0032]** A solution of 44 wt.% of trimethyl(2-hydroxyethyl)ammonium hydroxide or choline in methanol to which 1% hydroxylamine acetate was added as stabiliser, was fed to the reformat leaving the reactor 1 prior to the feed-effluent exchanger 5 at a dosage rate of 4,5 ppm per ppm chloride based on mass flow-rate, as indicated by the arrow 14 in the figure.

**[0033]** Pilot data have shown that the corrosion due to ammonium chloride can be reduced to levels below 1,270 mmpy (millimeter per year = 5 mpy or mills per year) and fouling created by ammonium chloride can be eliminated completely.

**[0034]** Also the amount of RCI (organic chloride) fed to the reactor could be reduced by 40 % as demonstrated through the analyses of CH<sub>3</sub>Cl in the recycle gas stream.

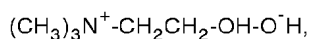
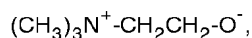
Product Analysis	Feedstock in ppm	Reactor Outlet Reformate ppm	Stabiliser feed Ppm	Recycle gas Ppm	Stabiliser off-gas Ppm	Stabilised reformat Ppm
NH <sub>3</sub>	1,5	-	-	-	-	-
HCl	0,5	-	-	-	-	-
NH <sub>4</sub> Cl	-	2,5	<0,1	<0,1	<0,1	<0,1
CH <sub>3</sub> Cl	-	-	< 0,1	1,1	<0,1	<0,1
RCI	2*	-	-	-	-	-

\*Organic chloride fed to reactor

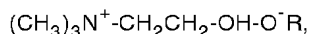
Analysis/ Observation	Hydrogen recycle airfin cooler	Stabiliser overhead airfin Cooler	Stabiliser overhead water cooler	Stabiliser overhead accumulator
Corrosion rate	0,076 mmpy (3 mpy)	0,058 mmpy (2 mpy)	0,102 mmpy (4 mpy)	0,038 mmpy (1,5 mpy)
Salt deposition	No	No	No	No
PH saturated water	6,3	7,6	7,0	7,1

[0035] The additive can be applied under a wide range of temperatures and pressures, usually between 0,02 bar<sub>a</sub> and 200 bar<sub>a</sub> and - 10 °C and + 250 °C.

[0036] In other embodiments, the additive was a derivative of choline with the general formula



or



wherein R = an alkyl with C<sub>1</sub>-C<sub>20</sub>.

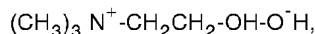
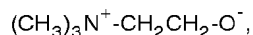
such as a choline hydrogen tartrate, choline dihydrogen citrate, tricholine citrate or choline gluconate.

[0037] Dosages are usually determined through the analysed or calculated concentration of ammonia and hydrochloric acid, or by dew point calculations of the sublimation of ammonium chloride or ammonium sulphates. The dosage could be as low as 1 mg/l up to 5000 mg/l.

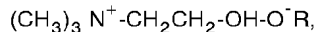
## Claims

1. Method for preventing fouling and corrosion caused by ammonium chloride and ammonium sulphates, **characterised in that** it comprises injecting as an additive a choline or a derivative thereof.

2. Method according to claim 1, **characterised in that** a choline derivative is added with one of the following general formulas:



and



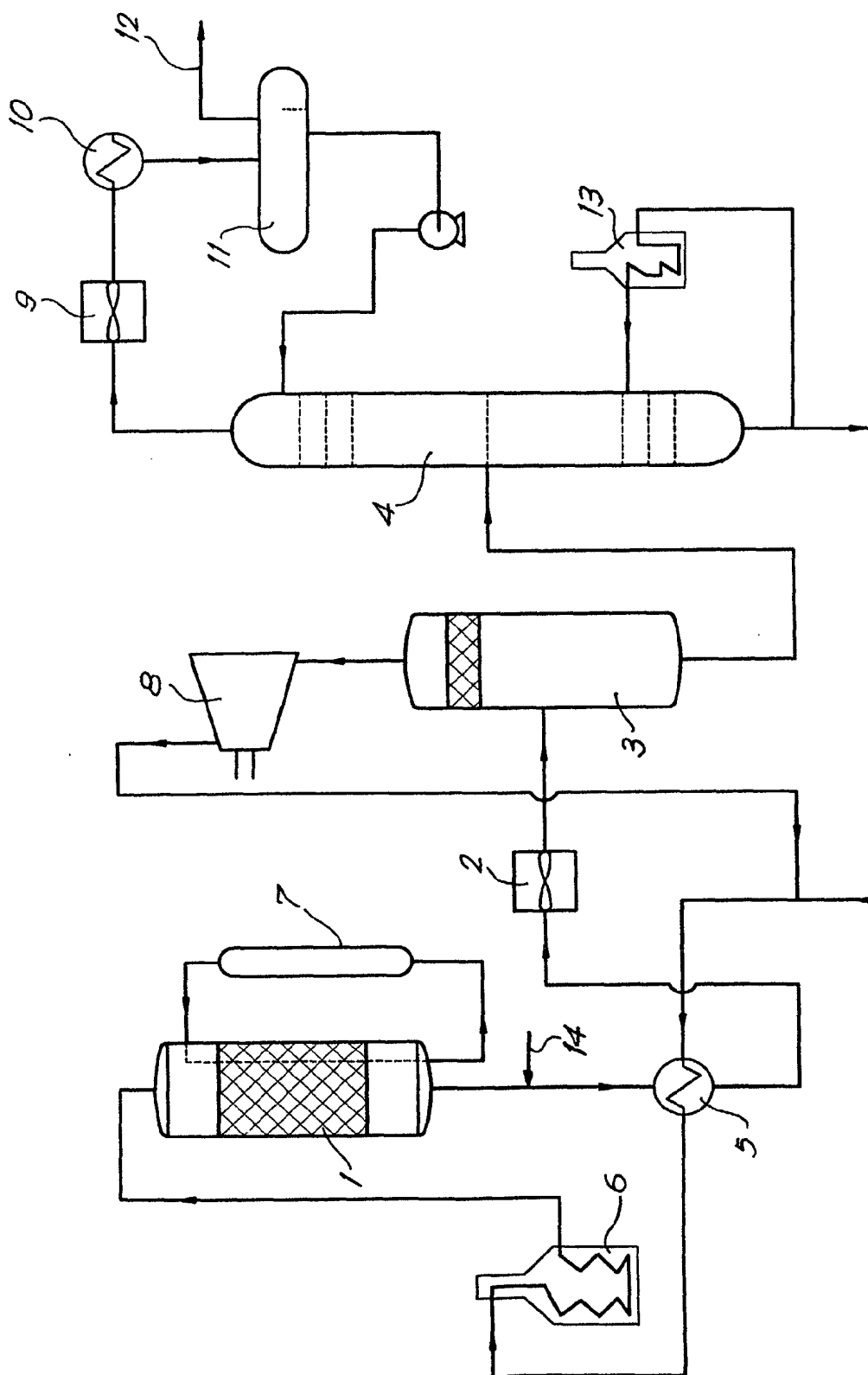
wherein R = an alkyl with C<sub>1</sub>-C<sub>20</sub>.

3. Method according to claim 1 or 2, **characterised in that** the volatile component formed by the additive is removed by stripping or gas recycling.

4. Method according to any one of the preceding claims, **characterised in that** it is used in a crude oil refinery process.

## EP 1 298 185 A1

5. Method according to claims 3 and 4, **characterised in that** it is used in a catalytic reformer, and the volatile component formed by the additive is recycled through the hydrogen recycle gas stream.
6. Method according to claim 4 or 5, **characterised in that** the additive is injected in an oil stream at a process pressures between 0,02 bar<sub>a</sub> and 200 bar<sub>a</sub> and a temperature between -10 °C and +250 °C.
7. Method according to any one of the preceding claims, **characterised in that** the quantity of additive injected is situated between 1 ppm and 5000 ppm, dosed on the amount of chlorides or sulphates present.
8. Method according to any one of the preceding claims, **characterised in that** the additive is injected as a solution containing 1% weight to 65 % weight additive in a solvent.
9. Method according to claim 8, **characterised in that** a solution of choline or a choline derivative in an alcohol, an ether, an aromatic or water.





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 01 20 3659

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 256 276 A (WEAVER CARL E) 26 October 1993 (1993-10-26) * column 1, line 15 - column 2, line 63; claim 1 *	1,4,7	C10G9/16
Y	US 5 965 785 A (MURPHY CHRISTOPHER J ET AL) 12 October 1999 (1999-10-12) * column 1, line 27 - line 38 * * column 6, line 1 - line 12; examples 3,4 * * column 5, line 1 - line 3 *	1,2,4,6-9	
Y	US 4 600 518 A (RIES DONALD G ET AL) 15 July 1986 (1986-07-15) * column 1, line 12 - column 2, line 14; table 1 *	1,2,4,6-9	
A	US 6 103 100 A (HART PAUL R) 15 August 2000 (2000-08-15) * column 11, line 33 - line 47 *	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C10G
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>13 February 2002</b>	Examiner <b>Deurinck, P</b>
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EP 01 20 3659 (P46G11)



**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 20 3659

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-02-2002

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5256276	A	26-10-1993	NONE		
US 5965785	A	12-10-1999	US	5714664 A	03-02-1998
			AU	682054 B2	18-09-1997
			AU	7416394 A	13-04-1995
			BR	9403883 A	13-06-1995
			CN	1118870 A ,B	20-03-1996
			EP	0645440 A2	29-03-1995
			JP	7180073 A	18-07-1995
			SG	50694 A1	20-07-1998
US 4600518	A	15-07-1986	CA	1266263 A1	27-02-1990
US 6103100	A	15-08-2000	AU	4577999 A	24-01-2000
			EP	1093507 A1	25-04-2001
			WO	0001785 A1	13-01-2000

EPO FORM P459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82